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LASER SPECTROSCOPY OF GLASSES

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LASER SPECTROSCOPY OF GLASSES

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Laser spectroscopy unlike most other spectroscopies used to study amorphous solids involves selective excitation of subsets of ions and molecules having electronic transitions resonant with the laser frequency. Thus by using a tunable laser, site-to-site variations in the distribution of environments and interactions present in a glass can be probed. High resolution, highly sensitive techniques such as laser-induced fluorescence line narrowing, spectral hole burning, and coherent optical transients are providing new insights into the spectroscopy and microscopic structure of glasses. Basic principles and recent results achieved with these unique techniques are reviewed.

INTRODUCTION

Lasers have revolutionized numerous spectroscopies. The application of laser techniques to investigations of solids, and amorphous materials in particular, has expanded greatly during the past decade. With spectral and temporal resolutions now measured in kilohertz and femtoseconds, lasers offer sensitive, highly selective spectroscopic probes of the local structure and interactions in glasses.

Because of the randomness of the local environment in glass, there is a distribution of physically different sites. Various spectroscopies such as magnetic resonance, diffraction, vibrational and Mössbauer spectroscopy yield information about glass structure. By using methods such as isotopic substituted neutron diffraction, x-ray absorption fine structure and anomalous dispersion, these spectroscopies can be atom specific. The measured quantities, however, still involve a weighted summation over an ensemble of individual sites.

A distinguishing feature of laser spectroscopy is that it is site or energy selective. Only ions or molecules in sites having electronic transitions resonant with the laser frequency are excited and observed. By using a narrowband tunable laser, an entire distribution of sites can be interrogated. This yields a wealth of spectroscopic information not previously available using conventional optical spectroscopy or other, more diverse spectroscopies.

Laser spectroscopy encompasses measurements in both the frequency and time domains. The former includes steady-state and time-resolved fluorescence line narrowing and spectral hole burning in which the frequency is scanned during the measurement; the latter includes coherent transients, such as optical free induction decays and photon echoes, measured as a function of time at fixed frequency. Because of the special experimental equipment and techniques required, initial developments in laser spectroscopy were mainly the province of physicists and chemists. Today's increased availability of suitable

lasers and well-established experimental techniques have opened the application of laser spectroscopy to a wider community of glass scientists.

The various experimental techniques cited above and their application to the investigation of glasses are described below. A general review of laser spectroscopy of solids covering history, techniques, and applications is presented in Ref. 1. Here we concentrate on more recent advances and applications to glasses. Laser spectroscopy has been used to investigate both organic and inorganic glasses. Early developments in these two areas proceeded independently, reflecting different interests and concerns, although recently there has been more commonality. References 2-4 provide reviews of the extensive laser spectroscopy devoted to studies of molecules in organic glasses and solutions. This brief review will concentrate on inorganic glasses.

BASIC PRINCIPLES

Probe Ions and Linewidths

Laser absorption and emission spectroscopy require the presence of optically active ions. These ions may be a component of the glass or, more commonly, a dopant, usually in the role of a network modifier. Dopant concentrations of $\tilde{<}1\%$ are generally sufficient, hence their effects on the glass composition and macroscopic properties are small. Depending upon the size and valence of the dopant ion, the local environment may be altered from that of the undoped glass, thus its value as a probe of intrinsic glass structure may be compromised. But for most absorption and luminescence applications, it is the local environment at the activator and how it varies from site to site that are of interest and this is precisely what is probed by tunable laser spectroscopy.

In a crystal where all sites are equivalent, the linewidth of an optical transition is determined by the natural or homogeneous linewidth $\Delta\nu_h$. In a strained or disordered medium, site-to-site differences in

local structure and fields result in different energy levels. If the extent of these differences is in the order of or greater than the homogeneous linewidth, the line becomes inhomogeneously broadened. An example of a continuous distribution of homogeneously broadening lines which overlap to form an inhomogeneous line profile of effective width $\Delta\nu_{ih}$ is shown at the top of Fig. 1. Inhomogeneous broadening is the bane of the spectroscopist seeking detailed information about specific sites in glass.

To achieve spectral site selectivity, $\Delta\nu_h$ should be much less than $\Delta\nu_{ih}$. One group of transitions and ions that satisfy this criterion are the 4f-4f transitions of the rare earths. The linewidths at low temperatures can be kilohertz or less compared to inhomogeneous linewidths of $\gtrsim 10^{12}$ Hz. Trivalent europium has been widely used as a probe ion because of several attractive features: the $^7F_0$-$^5D_0$ transition is a singlet, the crystal-field splittings of the $^5D_0$-$^7F_1$ and $^7F_0$-$^5D_1$ transitions yield simple triplets, the intensities of the $^5D_0$-$^7F_2$ and $^7F_0$-$^5D_2$ transitions are very sensitive to changes in the local symmetry and bonding, and these optical transitions are in readily accessible ranges for tunable dye laser excitation. Other rare-earth ions (Pr^{3+}, Nd^{3+}, Sm^{3+}, Yb^{3+}), transition metal ions (Cr^{3+}, Mo^{3+}) and post transition group ions (Bi^{3+}) have also been used for laser spectroscopy of glasses.[5] The ion-phonon coupling for 4f states of rare earths is weak, thus vibronic and multiphonon sideband intensities are very low.[6,7] This is in contrast to other transition group elements and molecules in organic glasses where sharp zero-phonon transitions are accompanied by broad, intense vibronic sidebands which overlap for different sites and hence are less useful for site selective spectroscopy.

Fluorescence line Narrowing

If a broadband source is used to excite fluorescence in glass, all ions are excited and an inhomogeneously-broadened emission line such as shown at the top of Fig. 1 is obtained. If, instead, a laser is used

for excitation, only those ions resonant with the laser frequency are excited. The fluorescence from this subset of ions, if observed in a time short compared to any spectral cross relaxation to other ions, will be narrow as shown at the bottom of Fig. 1. When $\Delta\nu_h << \Delta\nu_{ih}$, the line-narrowed fluorescence has a width $2\Delta\nu_h$ (because both excitation and emission processes are involved) plus any instrumentation width caused by the laser linewidth or the resolution of the detection system.[8] The first reports of laser-induced fluorescence line narrowing (FLN) in inorganic[9] and, independently, in organic[10] glasses appeared in 1972. The power of tunable lasers combined with FLN to investigate site-to-site variations in energy levels and transfer rates was demonstrated by Motegi and Shionoya in the following year.[11] The potential for further applications to glass studies was quickly recognized and the proliferation of investigations began,[12,13]

The line-narrowed fluorescence in Fig. 1 is resonant with the laser frequency. Nonresonant fluorescence transitions also exhibit line narrowing and avoid the problem of scattered laser light at the detection wavelength. This is illustrated in Fig. 2 where the $^5D_0 \rightarrow {}^7F_1$ fluorescence triplet is shown following excitation into the $^5D_0$ level of Eu^{3+}. A strikingly large variation in the energy level splitting of the $^7F_1$ state is observed as the laser wavelength is tuned across the $^7F_0 \rightarrow {}^5D_0$ absorption profile.

The three fluorescence lines in Fig. 2 are narrowed but are not as narrow as for the resonant case because of accidental degeneracy of excitation levels for ions in different sites.[5] This results in residual inhomogeneous broadening, the degree of which depends upon the nature of the disorder in the material. If energy level splittings are described by a single strain or disorder parameter, the transition energy will be unique to a specific environment. If, however, the disorder requires many parameters to describe the energy levels, there may be little correlation between transition energy and site and accidental degeneracies can span the entire inhomogeneous width. In this case, FLN is more energy than site selective.

When pulsed excitation is used, site-to-site variations in radiative and nonradiative transition probabilities can be measured from the decay of the line-narrowed fluorescence.[14] In cases where the ion-phonon coupling is strong, very large differences in nonradiative decay probabilities, greater than 25, has been found from line-narrowed fluorescence decays.[15] Homogeneous linewidths in solids are usually dominated by lifetime broadening caused by rapid phonon relaxation processes, thus measurements of $\Delta\nu_h$ also yield information about the strength of ion-phonon coupling.

Vibronic sidebands, although weak for rare-earth $4f$-$4f$ transitions (~1% of the zero-phonon line intensity), have been studied to obtain information about local, site-dependent vibrational modes. Comparisons of laser-excited vibronic spectra with vibrational spectra observed by Raman and infrared spectroscopy show very clearly that different selection rules are operative.[6]

Several years ago, the widths of line-narrowed fluorescence transitions of rare earths in glasses at low temperatures were discovered to be two to three orders of magnitude larger and exhibited different dependences on temperature than those of the same rare earths in crystals.[16,17] These features were attributed to interactions with tunneling modes associated with two level systems (TLS). This work subsequently spawned intensive laser investigations of optical line widths in both organic and inorganic glasses.

At sufficiently high dopant concentrations, ions interact by multipolar or exchange forces giving rise to ion-ion energy transfer. In FLN experiments, this phenomenon appears as a time-dependent decrease or broadening of the line-narrowed fluorescence in Fig. 1 accompanied by an increase in fluorescence intensity elsewhere within the inhomogeneous line profile.[18] Since the range of ion separations for observable transfer between rare earths in these experiments typically extends 1-2 nm, this result is further evidence that there is no structural order on this scale in the glasses studied. The energy difference in the

transfer is conserved by phonons. Recent measurements of time-resolved FLN of Yb^{3+} in silicate glass at 4.2 K show little transfer for energy differences <5 cm^{-1} because of the small density of states for such low frequency phonons.[19]

Apparatus for conducting FLN experiments in glass continues to become increasingly common and available. Organic dye and color-center lasers and the possible addition of optical harmonic generators and parametric oscillators provide tunable sources for selective excitation of most fluorescing ions of interest. Fluorescence is detected with instrumentation similar to that used for conventional optical spectroscopy. Etalons are added for high resolution studies. The laser spectral width and stability are ultimate limits on the selectivity and homogeneous linewidths that can be measured.[1]

Hole Burning

A common feature of spectral hole burning is photostimulation of some process which depletes or displaces in frequency the optical absorption or emission associated with those sites in an inhomogeneous spectral distribution that are in resonance with an irradiating laser. Causes of hole burning include saturation, photochemical and photophysical processes.[4,20]

Saturation hole burning arises from transfer of ground or excited state population to other states and is illustrated at the top of Fig. 3. The hole width is $2\Delta v_h$. If the rate of burning is fast compared to the rate of relaxation which restores the population, then the hole can grow to deplete the entire population and spectral line. Examples include absorption followed by transfer to a metastable state or stimulated emission from an inverted population.[21] In general there is some temporal behavior associated with saturation hole burning. Hole filling occurs by normal relaxation processes or by energy transfer and spectral diffusion from other ions in the inhomogeneous line profile.

Photochemical hole burning (PHB) involves a change in the structure of the center by photoionization, photodissociation, formation of anion radicals, or other processes that remove absorbers from the spectral region under irradiation. The hole appearance and width are generally as shown in Fig. 3A. Photochemical hole burning has been studied extensively for molecules in organic glasses. The process can have a high burning efficiency and is an effective method for performing high-resolution, frequency-selective photochemistry.

In photophysical hole burning (commonly referred to as nonphotochemical [NPHB]), the photoproduct is redistributed within the inhomogeneous band profile and appears as an increase in absorption (antihole) at frequencies off resonance. This behavior is illustrated in Fig. 3B and has been observed for molecules in organic glasses[2] and for rare earths in inorganic glasses[22] and hydroxylated polymers.[23] If the glasses are retained at low temperatures in the dark, holes may persist many hours after cessation of irradiation with no profile change. The hole develops because of an optically induced rearrangement of the glass structure resulting in a decrease in the number of ions resonant with the laser and an increase of ions resonant elsewhere within the inhomogeneously broadening band.

Experimentally, holes in silicate glasses have been burned with cw dye lasers having intensities of ~1 W/cm^2 in spectral widths of ~2MHz.[24] Exposure times ranged from 10 seconds to 10 minutes for samples at liquid helium temperatures with hole depths growing to ~10% of the total absorption. Compared to PHB, the efficiency of NPHB is low and becomes less with increasing temperature. There is also clearly a distribution of burning efficiencies.[22] For fluorescing samples, weak holes can be detected from excitation spectra. In this method, after hole burning the irradiating laser is attenuated and scanned over the inhomogeneous band profile while monitoring the fluorescence intensity. Care must be taken in selecting burning times and intensities to avoid anomalous effects caused by laser heating and saturation.

The width of the hole burned by excitation into the lowest crystal-field level of a rare earth J-state manifold is a measure of lifetime broadening caused by relaxation to lower-lying levels. For example, relaxation times of ~100 ps have been measured for Nd^{3+} in a silicate glass.[22] Hole burning becomes more difficult and hole widths increase for excitation into higher-lying crystal-field levels of the manifold because of more rapid relaxation. Hole burning efficiencies for Pr^{3+} and Nd^{3+} are two-to-three orders of magnitude higher in polymers than in inorganic glasses and show order-or-magnitude larger hole widths.[23]

In addition to spectral hole burning, polarization hole burning also occurs. Due to the random orientation of low-symmetry sites in glass, some ions interact more strongly with certain directions of the radiation field. Selective excitation of certain orientations leads to hole burning in the site distribution of cross sections and creates polarization-dependent line profiles. These effects have been observed in laser glasses and inhomogeneously broadening color-center bands.[21,25]

Coherent Transients

A third category of laser spectroscopy involves the time rather than the frequency domain and are extensions of pulsed magnetic resonance techniques to studies of optical dynamics.[26,27] Resonant excitation of a system of ions by coherent light creates a superposition of states and a macroscopic polarization. When the excitation is removed the system radiates a coherent beam of light in the form of free induction decays (FID) or, for multiple pulse excitation, photon echoes. Damping of these coherent optical transients provides a sensitive measure of interactions and dynamics within and between active centers.

The time and frequency domains are related by

$$\Delta \nu_h = \frac{1}{\pi T_2}, \qquad (1)$$

where $1/T_2 = 1/2T_2 + 1/T_2^*$. T_1 and T_2^* are the longitudinal and transverse relaxation times for the diagonal (population) and off-diagonal (pure dephasing) elements of the density matrix for the system. Both T_1 and T_2^* processes destroy phase coherence and contribute to the homogeneous linewidth.

For observation of optical free induction decays, the laser linewidth must be narrower than $\Delta\nu_h$. This entails complex laser stabilization and feedback techniques which, however, are within the present state of the art.[27] With extremely narrow cw laser linewidths, only a very small energy range of optical sites are sampled within the inhomogeneous line and site-to-site variations in dephasing times can be studied. Very fast dephasing times, however, limit the applicability of FID.

For the photon echo technique, the laser linewidth can be broader than $\Delta\nu_h$, thus relieving the most stringent requirement of FID, but now one necessarily averages over many sites and loses the site-to-site selectivity. In the accumulated photon echo technique,[28] a sample is irradiated by a train of picosecond pulse pairs from a synchronously-pumped, mode-locked dye laser. The separation τ between pairs of pulses is variable. One pair of pulses creates a population grating in frequency space with a periodicity $1/\tau$ and one pulse from the next pair stimulates an echo. Signals build up by storage of population in a metastable energy level. A well-defined phase relationship is needed between the optical field of the two pulses. The echo decays as $\exp(-2\tau/T_2)$, where T_2 is related to $\Delta\nu_h$ by Eq. (1). The accumulated photon echo technique is powerful because $\Delta\nu_h$ can be measured over a large dynamic range, from ~5MHz to 50 GHz. It works well for weak fluorescing levels as long as an efficient population storage level exists. Picosecond accumulated echoes have been used to measure homogeneous linewidths of rare earths in inorganic glass[29] and of molecules in organic glasses.[2]

ADDITIONAL EXPERIMENTAL RESULTS

Laser spectroscopy, as just described, can measure distributions and site-to-site variations of energy levels, radiative and nonradiative transition probabilities, optical dephasing processes, and ion-phonon and ion-ion interactions in glass. Results and applications for inorganic glasses obtained through 1980 are reviewed in Ref 5. Here we describe selected recent developments which reveal some of the further power and usefulness of these new experimental techniques.

Variations in Microscopic Glass Structure

The FLN spectra in Fig. 2 show the existence of large site-to-site variations in crystal-field splittings of rare-earth ions in glass. Brecher and Riseberg,[30] in an early pioneering study, made extensive measurements of Eu^{3+} and derived crystal-field parameters from individual FLN spectra. They then sought a structural model of the rare earth environment which would account for the large spectral variations observed. Different geometric models of the nearest-neighbor coordination were required to explain the results for oxide and fluoride glasses.[31] Unfortunately, no uniqueness theorem exists to prove that these structural models are the only way to explain the FLN spectra.

In another approach, Brawer simulated the structure about the rare-earth ion in a glass using Monte Carlo[32] and molecular dynamics methods.[33] Each computer simulation yields a different structural arrangement; a large collection of such simulations should, if the process is meaningful, represent the range of environment present in an actual glass. Fig. 4 shows energy levels of Eu^{3+} in BeF_2 glass calculated from 160 simulated structures using a simple point charge model. The observed asymmetry of the $^5D_o-^7F_o$ transition, the inhomogeneous broadening and FLN spectra of the $^5D_o-^7F_1$ transition, the residual broadening due to accidental degeneracies of excitation levels, and changes in spectral intensities are all predicted by these studies.[34]

Although the above results are encouraging, the models are overly simplified and the simulated structures have recognized limitations in their validity.[35] As our ability to calculate crystal-field energy levels and spectral intensities of ions in glass improves, laser-excited spectra and lifetime measurements will provide a critical test of proposed structural models for ions in glass.

Phase Transformations and Nucleation

Laser spectroscopy provides a unique probe of changes in local structure and bonding in glasses, hence it can be used to detect and monitor changes caused by intrinsic transformations or those induced by externally applied conditions. Early FLN studies of alkali borate glasses using Eu^{3+} as a probe ion revealed spectral details and changes with alkali content not obtainable from conventional spectroscopy.[36,37] These glasses are of interest because of the known change in the oxygen coordination number for boron with alkali content and the existence of subliquidus immiscibility. In a recent study of Eu^{3+} in a sodium borate glass,[38] the $^5D_0 \rightarrow {}^7F_1$ FLN spectrum was monitored for glasses annealed below and above the glass transition temperature. The observed general narrowing of the $^7F_1$ splitting for the latter case was interpreted as due to segregate of Eu^{3+} ions in the sodium-poor phase.

Structural transformations associated with the gel-to-glass transition in low-temperature glass formation have also been investigated using Eu^{3+} FLN spectroscopy.[39]

In glass ceramics, a probe ion may, depending upon the composition and structure, be incorporated into the glassy or the crystalline phase or both. The shape and inhomogeneous broadening of absorption and emission lines of Eu^{3+} in phosphotungstate glass demonstrate that Eu^{3+} ions occur in both phases. Laser selective excitation has yielded further information about the phases.[40]

Microcrystallites develop in silicate glasses by heat treatment. For example, nucleation is induced by Cr^{3+} ions when cordierite glass is heated above 800°C. Site distributions and inhomogeneous broadening have been studied in this system by laser spectroscopy of the Cr^{3+} $^2E \rightarrow {}^4A_2$ transition.[41]

Tunneling Systems

Atomic tunneling systems (two-level systems) appear to be an intrinsic property of the amorphous condensed state. They are considered to be the cause of the anomalous magnitude and temperature dependence of the homogeneous linewidths noted earlier for paramagnetic ions and molecules in organic and inorganic glasses at low temperatures. Homogeneous linewidths have been determined from fluorescence line narrowing and spectral hole burning, however as the temperature is lowered to $\tilde{<}1$ K, coherent transients becomes a more convenient method to determine $\Delta\nu_h$ from direct measurement the optical dephasing rate T_2^{-1}. This has been demonstrated in two-pulse photon echo experiments of Hegarty, Broer, and coworkers for Nd^{3+} in SiO_2 glass fibers.[42] The results are described in terms of a spectral diffusion process in which the optical ions interact by elastic dipole-dipole interactions with tunneling systems.[43] The model was suggested by the similarity of the Nd^{3+} homogeneous linewidth in SiO_2 to the homogeneous linewidth of tunneling systems in SiO_2.

Laser Glass

Whereas selective excitation with lasers is advantageous for spectroscopic investigations of glass, selective de-excitation is deleterious for the operation of glass lasers. Inhomogeneities arising from site-to-site variations of energy levels and from randomly oriented dopant ions with anisotropic cross sections cause spectral and polarization hole burning in the gain profile. These effects have been known for many years and result in reduced gain and energy extraction efficiency. Glasses in which these effects are a minimum are obviously desired for high performance lasers operating in the large-signal (saturated) gain regime.

Information required to characterize laser glasses for large-signal gain operation can now be obtained from FLN experiments.[44] The phenomena of interest and measurement techniques required are summarized in Table I. These data have, in turn, been used to model hole burning and energy extraction efficiencies in actual laser amplifiers.[21,45]

CONCLUDING REMARKS

Laser spectroscopy of glasses is still a relatively new area of research. Numerous experimental techniques pioneered in recent years have expanded the tools available to explore spectral and dynamic properties of ions and molecules in glasses. Yet, except for a few isolated instances,[46,47] the range of glasses investigated thus far is small and not representative of the wide diversity of known glass forming systems. More systematic studies of energy levels and transition probabilities as a function of glass composition should increase our knowledge and understanding of the local structure and bonding at activator sites. In addition, probe ions should be selected to probe both glass former and glass modifier sites.

FLN data provides a critical test of models of microscopic glass structure. However, optical properties of ions and molecules are determined by both the local atomic arrangement and resulting electronic structure. At present we are incapable of performing ab initio calculations of optical properties combining these two features.[48] Thus the interpretation of FLN spectra in terms of a structural model is dependent on the adequacy of our treatment of the local field.

The persistent holes burned into the spectra of ions in inorganic glasses are an exciting discovery. These holes are attributed to photo-induced structural rearrangements, however the exact nature of these structural changes is not known. Further investigations are needed to understand the energetics of hole formation and relaxation, the details of thermal and photobleaching, and how these properties vary from site to site. In organic glasses, hole filling has been examined by burning a

neighboring hole, thereby obtaining information about the size of the resonance shift.[49] Computer simulations may also provide some insights into the structural changes occurring during hole burning by laser irradiation.

Optical dephasing in glasses at low temperatures, determined both in the frequency and time domains, appears to be dominated by interactions with a random distribution of tunneling systems. Numerous attempts have been made to account for the observed behavior theoretically.[50] The microscopic nature of two-level systems and how the disorder and other physical properties of glasses are related to these excitations are not understood. Laser spectroscopy should provide information useful in this quest.

Recent investigations of optical dephasing in organic amorphous systems have shown that one must be careful when comparing photon echo data with results of nonphotochemical hole burning. When spectral diffusion is dominant, the time scale of the experiment is important in determining the measured spectral width.[51]

Finally, we may expect further developments of existing laser techniques and the appearance of new techniques which may be applied to the study of glasses. For example, the contours of ultranarrow spectral holes have been measured using lasers and Doppler displacement analogous to what is done in the Mössbauer effect.[52] Further applications of sequential absorption of two or more photons should enhance site selectivity in both FLN and hole burning experiments. Site selection spectroscopy was reported recently using three tunable input frequencies in a nonlinear four-wave mixing scheme applicable to non-emissive samples.[53] These and other sophisticated nonlinear laser spectroscopy techniques[54] should find increasing use in studies of glasses.

ACKNOWLEDGMENT

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TABLE I. Phenomena and properties affecting the large-signal gain of laser glass.

Property	Measurement Technique
Spectral Hole Burning:	
Homogeneous linewidth	Resonant FLN spectrum
Inhomogeneous linewidth	Fluorescence spectrum
Polarization Hole Burning:	
Cross section anisotropy	Polarized FLN spectra
Hole Filling:	
Cross relaxation rates	Time-resolved FLN

FIGURE CAPTIONS

Figure 1   Principles of inhomogeneous broadening and laser-induced fluorescence line narrowing. Top - inhomogeneously broadened line profile; bottom - resonant laser-excited fluorescence. $\Delta\nu_{homo}$, $\Delta\nu_{inhomo}$ and $\Delta\nu_{instr}$ are the homogeneous, inhomogeneous and instrumentation line widths.

Figure 2   Partial energy level scheme for Eu^{3+} and nonresonant $^5D_0 \rightarrow {}^7F_2$ FLN spectra as a function of $^7F_0 \rightarrow {}^5D_0$ excitation energy for a silicate glass at 77 K.

Figure 3   Spectral hole burning in an inhomogeneously broadened transition. The dashed curve denotes the original line profile. (A) Hole burning caused by saturation or photochemical processes. (B). Nonphotochemical (photophysical) hole burning.

Figure 4   Site-to-site variations of the energy levels for EU^{3+} in BeF_2 glass calculated from computer-simulated structures and a point-charge model. Sites are ordered by increasing $^5D_0 \rightarrow {}^7F_0$ energy (the $^5D_0$ energy is held constant for all sites).

Inhomogeneously broadened fluorescence

Δv_{inhomo}

Δv_{homo}

Line-narrowed fluorescence

v_{laser}

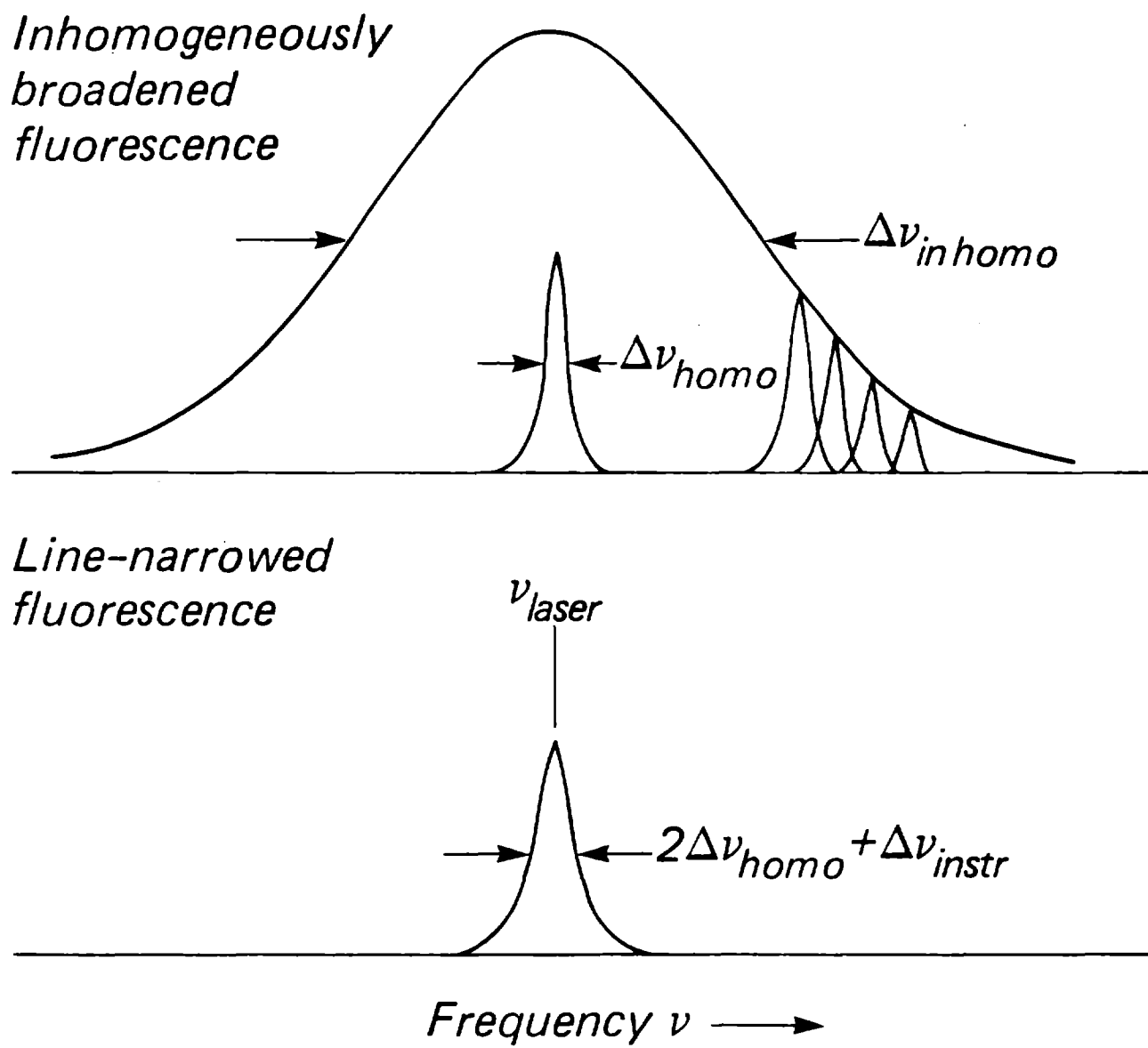$2\Delta v_{homo} + \Delta v_{instr}$

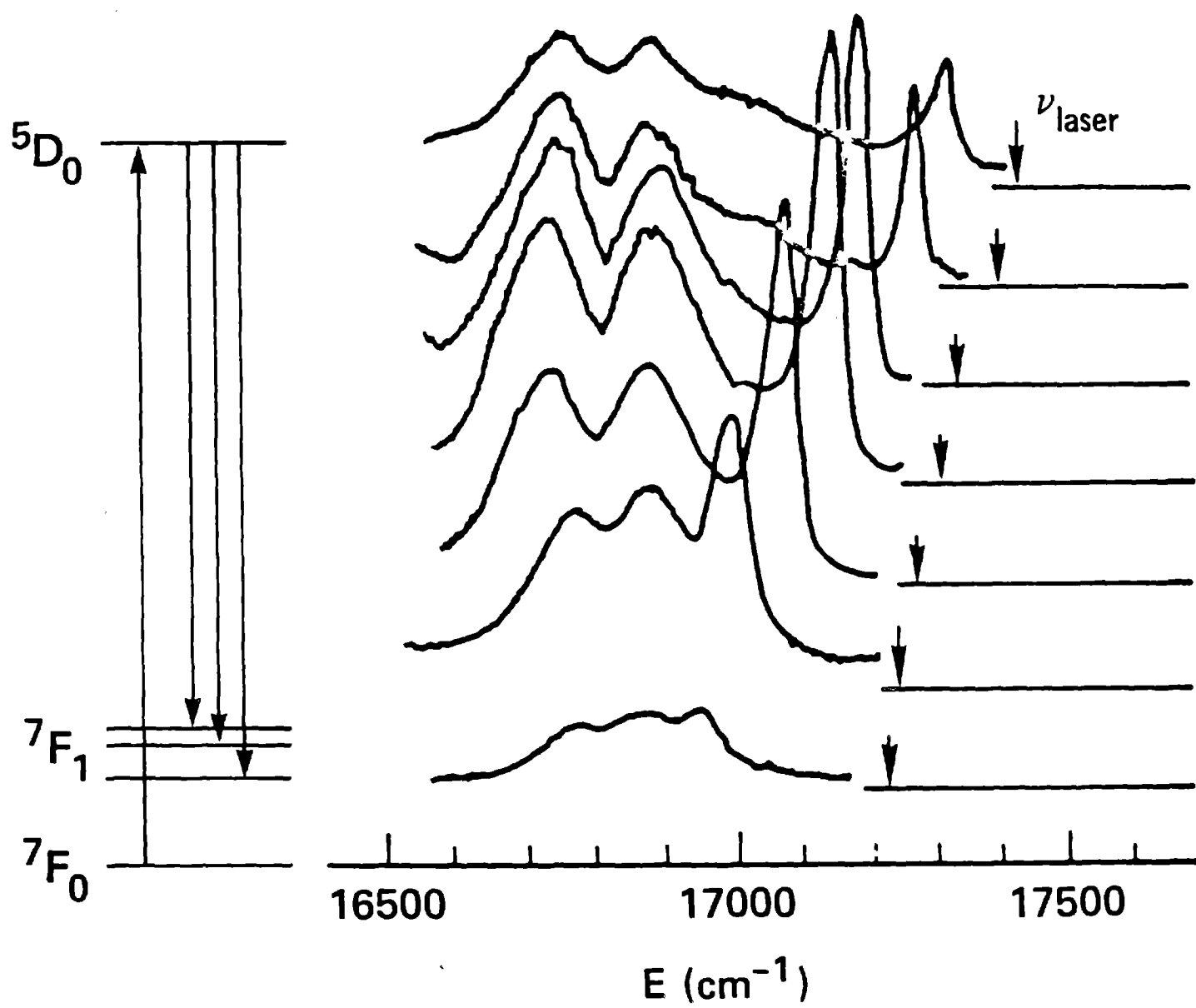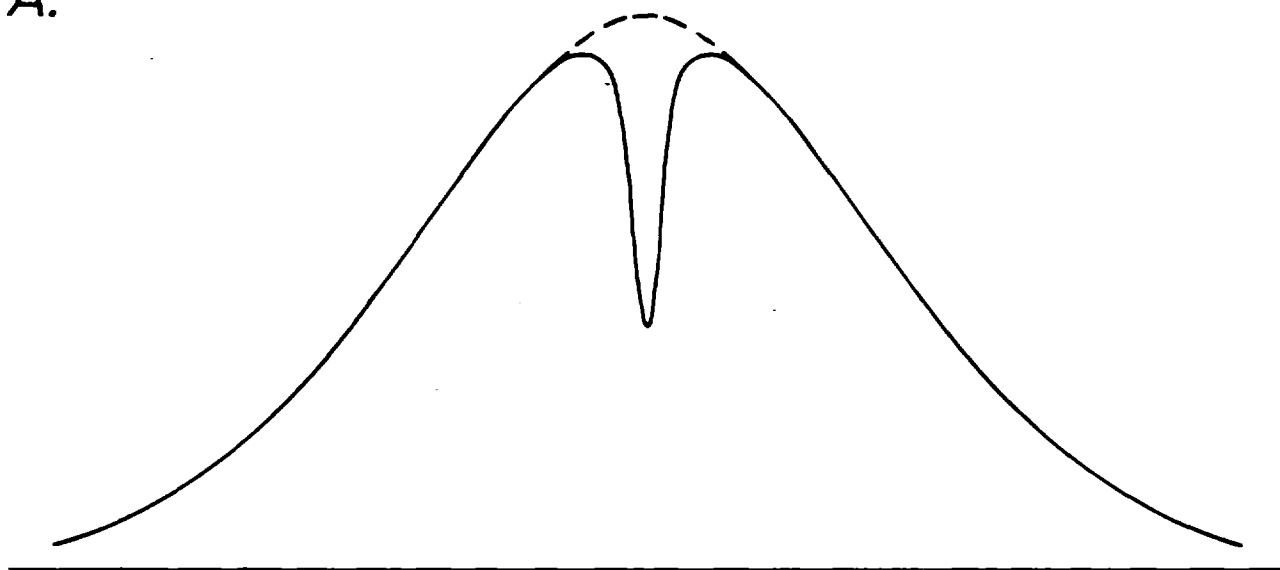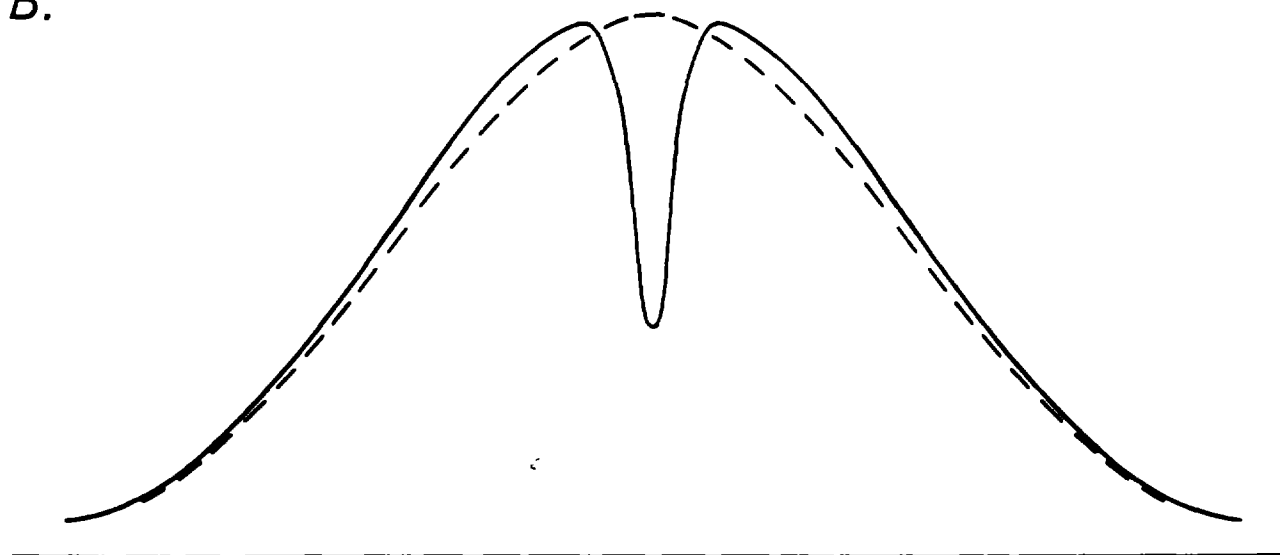Frequency $v \longrightarrow$

Figure 1

Figure 2

Spectral hole burning

A.

B.

Frequency ⟶

Figure 3

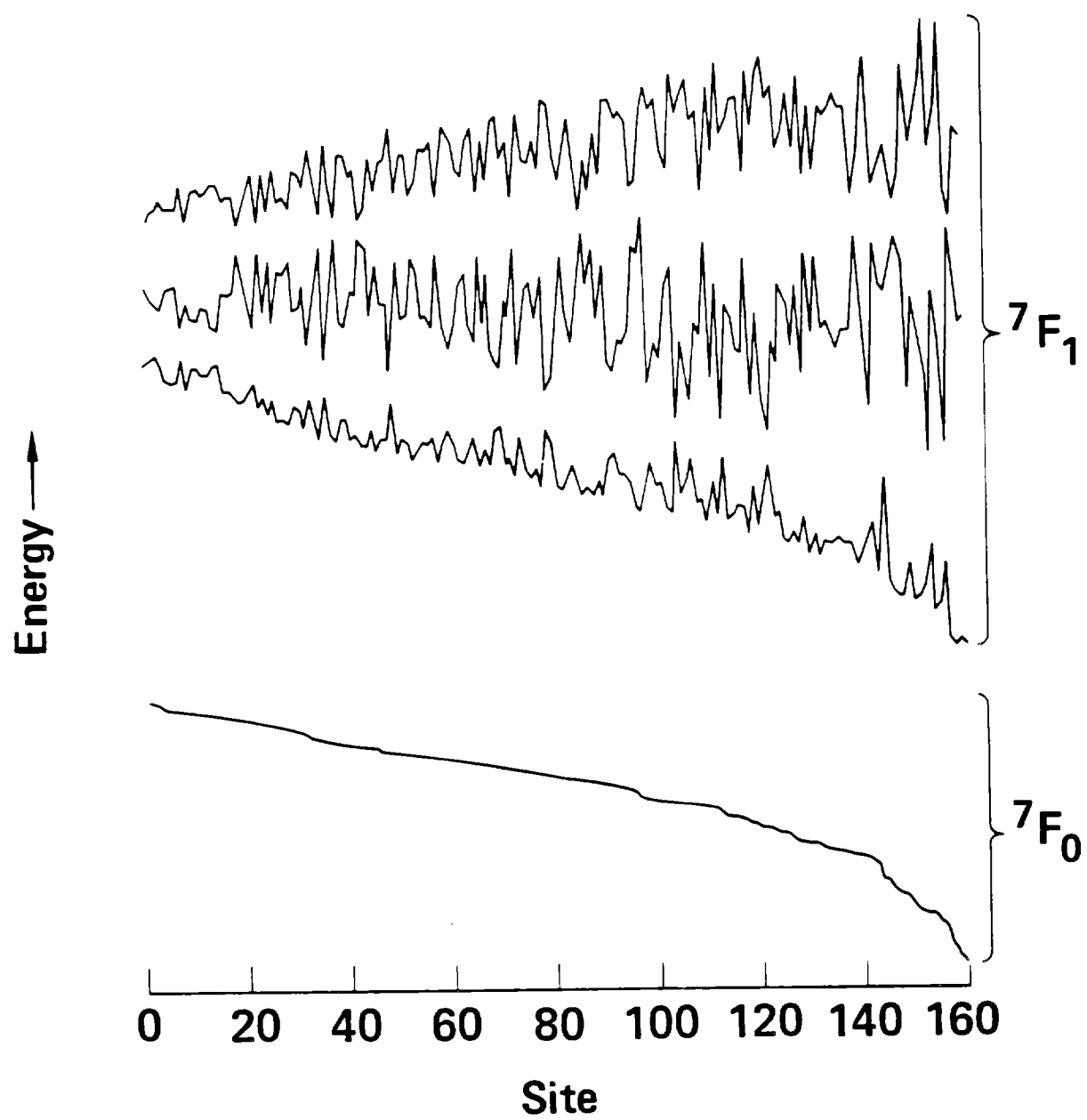Figure 4